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Mikhnenko, Oleksandr V.; Blom, Paul W. M.; Loi, Maria Antonietta

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COMMUNICATION

Sensitive triplet exciton detection in polyfluorene using Pd-coordinated porphyrin

Oleksandr V. Mikhnenko,*[ab] Paul W. M. Blom[ac] and Maria Antonietta Loi*[a]

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We developed a sensitive spectroscopic method to probe triplet concentration in thin films of polyfluorene (PF) at room temperature. The energy of photoexcited triplet excitons is transferred to the guest metal–organic complex, *meso*-tetratolylporphyrin-Pd (PdTPP), and detected as phosphorescent emission. The phosphorescence intensity of PdTPP–PF blends is proportional to the independently measured triplet concentration using photoinduced absorption experiments. The high sensitivity of this method allows room temperature detection of triplet excitons in spin-coated polymer films as thin as 10 nm. We found that the triplet lifetime is independent of PdTPP concentration and therefore this method is nearly *non-perturbing* for the triplet population.

Introduction

To design highly efficient optoelectronic devices, a thorough understanding of the physics of triplet excitons in organic semiconductors is required. According to spin statistics, 75% of all electron–hole pairs form triplet excitons in an organic light emitting diode (OLED). Since organic materials consist of rather light atoms with weak spin–orbit interactions, the radiative transitions of triplets—phosphorescence—are usually inefficient. To extract the energy of triplet excitons as light output, the triplets should be manipulated toward phosphorescent emitting systems[1–4] or extracted as delayed fluorescence.[5] Recently, it has been pointed out that also in solar cells the transformation of singlet to triplet excitons can significantly enhance the power conversion efficiency.[6–9] Furthermore, the reverse to the triplet–triplet annihilation process, singlet fission, shows great potential for further optimization of solar cells.[10,11] The physical processes that influence the device performances include diffusion, triplet–triplet annihilation, singlet fission, and triplet–polaron interactions. Experimental approaches to study these processes relay on the detection of triplet excitons. In particular, it is very important to detect triplet excitons at low densities, below the triplet–triplet annihilation threshold, to access the intrinsic properties of triplets such as triplet exciton diffusion.

[a] *Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: alex@mikhnenko.com, m.a.loi@rug.nl*
[b] *Dutch Polymer Institute, P.O. Box 902, 5600 AX, Eindhoven, The Netherlands*
[c] *Holst Centre, High Tech Campus 31, 5656 AA, Eindhoven, The Netherlands*

However, detection of low triplet concentrations is very challenging at room temperature in ultra thin films using the conventional methods such as phosphorescence spectroscopy or photoinduced absorption. At room temperature triplet lifetime is usually one order of magnitude shorter than at liquid nitrogen temperatures.[1,12–15] Consequently both phosphorescence and photoinduced absorption signals are difficult to detect. Furthermore, the phosphorescence intensity and absorption of the triplet excited state are proportional to the film thickness. Generally, if the sample thickness is of the order of 100 nm, which is a typical active layer thickness for OLEDs and organic solar cells, the application of these methods at room temperature requires high laser intensities and high triplet densities, usually well above the triplet–triplet annihilation threshold. Thus it is important to develop alternative sensitive methods to detect low concentrations of triplet excitons in device configurations.

Doping organic semiconductors with metal–organic complexes can allow the phosphorescent detection of the triplet excitons. A triplet that is initially generated in the organic semiconductor can be transferred to the dopant complex.[16–21] Owing to high atomic number of the metal, such as palladium, iridium *etc.*, the spin–orbit coupling of the complex is relatively large enabling the efficient radiative recombination of the transferred triplet exciton. However, the triplet harvesting by metal–organic complexes is capable to strongly perturb[22] the triplet population of the host material and influence processes such as triplet–triplet annihilation.[3]

Here we present a nearly *non-perturbing* sensitive detection of low triplet densities in ultra-thin films of a conjugated polymer at room temperature. We have chosen poly(9,9-di-*n*-octylfluorene) (PFO) as a model polymer with high potential for applications in optoelectronic devices such as light emitting diodes and lasers.[23] We show that the palladium-coordinated porphyrin, *meso*-tetratolylporphyrin-Pd (PdTPP), can be used as non-perturbing phosphorescent sensor of triplet excitons in PFO. This porphyrin molecule is photochemically stable, has sharp absorption bands, long phosphorescence decay time and appropriate energy level alignment with PFO.

Experimental methods

Poly(9,9-di-*n*-octylfluorene) (PFO) was synthesized by the Netherlands Organisation for Applied Scientific Research (TNO);

meso-tetratolylporphyrin-Pd (PdTPP) was purchased from Porphyrin Systems; poly(methyl methacrylate) (PMMA) and polystyrene (PS) were acquired from Aldrich. The materials have been used without further purification. All sample fabrication steps including preparation of solutions, filtering, drop-casting and spin-coating were done under a nitrogen atmosphere in a glove box. A drop-casting technique has been used to prepare PdTPP blends with PFO, PMMA and PS as well as to prepare ~1–2 μm PFO film for photoinduced absorption experiments. 10 nm films of PFO and PMMA have been spin-coated at 2000 rpm. The sublimation of PdTPP was performed in high vacuum with pressure lower than 2×10^{-7} mbar, at a deposition rate of 0.04 Å s^{-1}. Samples for spectroscopic measurements were mounted in an optical cryostat and kept under vacuum of 5×10^{-5} mbar. Absorption spectra were measured by a Perkin-Elmer spectrometer under ambient conditions. Polymer thickness was measured by a Dektak profilometer and an atomic force microscope.

The set-up for photoinduced absorption (PIA) experiments consists of an argon laser operating at 466 nm, a tungsten lamp, a monochromator and a low noise silicon photodetector. A mechanical chopper was used to modulate the pump laser. The signal was further amplified using a phase sensitive detector. The dependence of the triplet PIA band intensity on the modulation frequency was measured with a Hamamatsu photomultiplier tube (PMT) loaded with a small resistance to ensure fast response in the modulation range of 40–2000 Hz.

The photoluminescence/phosphorescence spectra were recorded by the PMT in combination with a monochromator. As for PIA experiments the laser excitation at 466 nm was modulated by a mechanical chopper and the signal was enhanced by a lock-in amplifier. The phosphorescence decay time of PdTPP was measured with PMT directly linked to a digital oscilloscope.

The laser power was controlled by a circular variable neutral density filter and a power meter, which was connected with a computer to record the light intensity directly during the measurements. Each power dependence measurement has been swept from the highest to the lowest excitation power, followed by the back scan from the lowest to the highest. The back scan did not show notable degradation of the signal in all reported experiments. The incident power density was determined by dividing the total laser intensity over the circular area of the Gaussian beam waist radius. The beam waist was measured using pin holes of various sizes and found to be about 55 μm for the used experimental set-up.

Results and discussion

Fig. 1 shows the photoluminescence/phosphorescence spectrum of PdTPP film deposited by vacuum sublimation on top of a spin-coated layer of PMMA. The PdTPP thickness was controlled by the quartz thickness monitor during the sublimation and was set to 1 nm. The PMMA is a wide band gap material and plays the role of an inert flat substrate. The excitation wavelength of 466 nm was detuned from the absorption maxima of PdTPP. Three weak peaks at 620 nm,

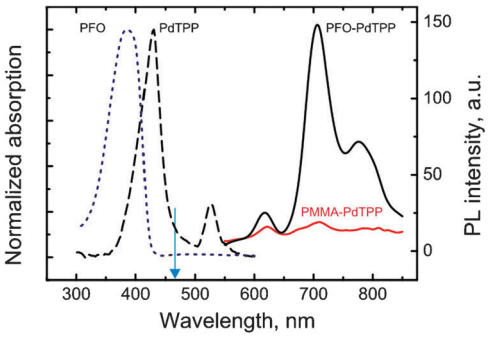

Fig. 1 Absorption spectra of PFO (dotted) and PdTPP (dashed). Photoluminescence spectra of two layer heterostructures PFO–PdTPP and PMMA–PdTPP are plotted as solid lines. The excitation wavelength at 466 nm is marked with the arrow.

670 nm and 700 nm are resolved in the emission spectrum of PdTPP. Only the peak at 700 nm is attributed to phosphorescence with a decay time of the order of a millisecond; the other peaks appear to be the prompt photoluminescence of PdTPP. It is important to note that the intensity of phosphorescent emission was as weak as that of photoluminescence also when PdTPP was deposited on clean quartz substrates regardless of the film thickness, which was varied in a wide range up to 1 μm.

The PL spectrum of PdTPP film, sublimed under the same conditions on top of a 10 nm thick spin-coated PFO film, is also plotted in Fig. 1. Remarkably, the phosphorescent intensity of the PdTPP layer is one order of magnitude higher when deposited on top of PFO as compared to the PMMA–PdTPP heterostructure. The increase in phosphorescent intensity indicates that PFO acts as an antenna to collect optical excitations for PdTPP. Below we will show that the enhanced phosphorescence of PdTPP is mainly due to optically generated triplet excitons in a PFO layer that are transferred to PdTPP.

The inset in Fig. 2 shows the photoinduced absorption spectrum of a 2.5 μm thick drop-casted PFO film. The spectrum was acquired at room temperature and consists of a distinct peak at ~1.45 eV with a shoulder on the higher energy side. The detected feature is typical[12,24] for the T1–Tn transition in PFO and its intensity is proportional to the product of the sample thickness, the concentration and

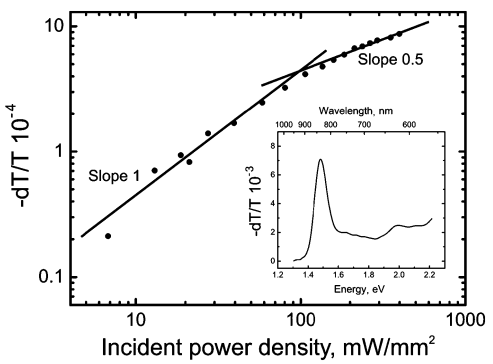

Fig. 2 Dependence of the maximum of the T1–Tn transition on the incident power density in PFO; sample was excited at 466 nm. The inset presents the photoinduced absorption spectrum.

the absorption cross-section of the triplet excited states.[1] The triplet exciton concentration is proportional to their lifetime that is relatively short at room temperature (0.1 ms), as compared with liquid nitrogen temperatures (1–7 ms, ref. 12). Consequently thick PFO film and high laser excitation power (500 mW mm^{-2}) are necessary to record the photoinduced absorption spectrum.

It is noteworthy that the laser excitation at 466 nm is able to generate triplet excitons in ample concentration to have triplet–triplet annihilation in PFO. The corresponding photon energy of 2.66 eV is just above the triplet energy of 2.3 eV.[1,13,25] On the other hand, the polymer's optical gap is about 3–3.2 eV. The mechanism of triplet exciton generation under such conditions can be understood from considerations of the density of states (DOS). Due to the disordered nature of the polymer, excitonic density of states is rather broad and can be described with a Gaussian distribution. Singlet excitons can be generated at the low energy tail of the DOS in our experiments. Those excitons can undergo intersystem crossing to generate triplets.

Fig. 2 illustrates the dependence of the T1–Tn transition peak intensity on the incident power density. At low excitation densities the triplet peak increases linearly with the incident laser power. Above ~100 mW mm^{-2} its intensity scales as square root of the supplied power. On the log–log graph these two regimes appear as branches with slopes 1 and 0.5, respectively.

The non-linear dependence of the triplet peak intensity on the incident power density is determined by the triplet–triplet annihilation (TTA) phenomenon.[1] The probability that two triplet excitons meet each other during their lifetime is significant when their concentration is high. Once brought together two triplets (T^*) can undergo annihilation, which results in one singlet excited state (S^*) and one singlet ground state (S):

$$T^* + T^* \rightarrow S^* + S.$$

The TTA process introduces an additional decay path for triplet excitons that is responsible[14] for the slope of 0.5 on the log–log plot in Fig. 2.

Fig. 3 shows the dependences of the phosphorescent emission intensity of PdTPP at 700 nm under different power excitations in various sample configurations. All the data were first normalized to their maximum value and then displaced vertically for clarity. The upper five curves correspond to drop-casted samples of PdTPP blended with PFO in concentrations ranging from 0.05 wt% (top) to 60 wt%. The two lowest curves with a slope of 0.9 correspond to PdTPP blended into PMMA (pentagons) and PS (squares) with concentrations of 0.03 wt% and 0.1 wt%, respectively.

PFO acts differently as host material for PdTPP in comparison to PMMA or PS. A small amount of PdTPP blended into PMMA or PS reveals nearly linear dependence of the phosphorescent intensity on the incident power in the whole studied power range. On the log–log scale these dependences appear with a slope of ~0.9 (Fig. 3). In contrast, similar concentrations of PdTPP blended with PFO show two distinct regimes on the log–log plot, with slopes of 1 and 0.5 respectively. It is important to note that the photoluminescence

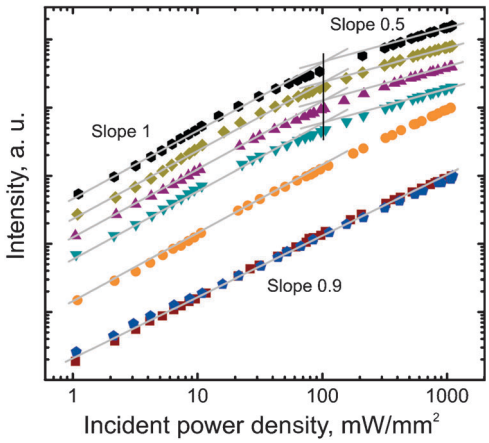

Fig. 3 The dependence of the phosphorescence intensity at 700 nm on the incident power density of PdTPP blended in PFO with the following concentrations, from top to bottom: 0.05 wt% (hexagons), 0.5 wt% (diamonds), 5 wt% (triangles), 25 wt% (triangles) and 60 wt% (circles). Laser excitation was at 466 nm. The data were first normalized to the value at the maximum incident power of 1000 mW mm^{-2} and then displaced vertically for clarity. The two dependencies with a slope of 0.9 correspond to PdTPP imbedded in the inert matrix of PMMA (pentagons) and PS blend (squares).

intensity of the PdTPP measured at 620 nm depends linearly on the incident power density in each blend, as does the PFO emission above 550 nm in the PdTPP–PFO sample (not shown here).

The comparison of Fig. 2 and 3 reveals that the phosphorescence intensity of PdTPP–PFO blends is proportional to the intensity of the independently measured triplet T1–Tn PIA band, which is proportional to the triplet concentration. In this way we demonstrate that PdTPP acts as a sensor of triplet excitons in PFO. The non-linearity of the phosphorescence intensity at high incident power densities is then governed by the triplet–triplet annihilation process within the PFO matrix. Triplet energy transfer is possible from PFO to PdTPP since the triplet level of PdTPP (1.8 eV) is below that of PFO (2.3 eV), the back transfer is energetically unfavorable.

To understand the impact of the PdTPP guest molecules on the triplet lifetime of PFO, blends of various PdTPP concentrations have been examined. Samples with PdTPP concentration of 25 wt% and lower show identical non-linearity at high excitation powers, which is represented by the slope of 0.5 on the log–log scale (Fig. 3). Only the sample with concentration of 60 wt% deviates from the general trend and resembles the dependency of the porphyrins in the inert matrix.

Fig. 3 demonstrates that the threshold laser power at which the dependence changes from a linear to non-linear regime is identical in wide range of concentrations from 0.05 to 25 wt%. This threshold power corresponds to the triplet density [T_{th}], above which the TTA is efficient. Furthermore [T_{th}] is determined by the triplet lifetime τ (ref. 1):

$$[T_{th}] \propto 1/\tau.$$

[T_{th}] is independent of the amount of PdTPP, consequently also is τ. Thus doping PFO with PdTPP does not lead to the reduction of the triplet lifetime. In this respect PdTPP *does not perturb* the triplet population in PFO. Our findings are in

agreement with studies reporting that the triplet lifetime in PFO is insensitive to the presence of Pt-coordinated porphyrins, which have similar phosphorescence decay time to PdTPP.[23,24]

The non-perturbing triplet detection can be further understood by comparing the lifetimes of the excited states. The phosphorescence decay time of PdTPP is 0.9 ms, as we measured in the PFO matrix. The triplet lifetime of PFO is estimated from the dependence of the intensity of the PIA band on the modulation frequency and fitted with the equation

$$-\mathrm{d}T/T \propto \frac{1}{\sqrt{1+(2\pi\tau f)^2}},$$

where f is the chopper frequency and τ is the triplet lifetime. At room temperature with an excitation density of 500 mW mm^{-2} it is equal to $\sim$0.1 ms, which is one order of magnitude smaller than that of the phosphorescence decay time of PdTPP. Thus under continuous wave excitation it takes at least 10 lifetimes/generations of triplets in PFO between possible energy transfer events to a PdTPP molecule. Consequently the triplets population is not perturbed by the presence of PdTPP.

Triplet excitons can be easily detected by PdTPP under experimental conditions that are particularly challenging for photoinduced absorption measurements, namely ultra thin films, room temperature and low excitation powers. The phosphorescence spectrum of the PdTPP–PFO heterostructure in Fig. 1 shows a strong emission at 700 nm, which we accordingly assign to detected triplets in the 10 nm thick PFO layer under an excitation of 50 mW mm^{-2}, that is well below the triplet–triplet annihilation threshold. Thus the proposed detection method is applicable to study triplet–triplet annihilation and other diffusion related processes in configurations appealing for practical applications.

Conclusions

In summary, we have shown highly sensitive triplet detection in ultra thin films of polyfluorene under low excitation densities and at room temperature. Under these conditions the conventional method of triplet exciton detection, photoinduced absorption is extremely challenging. Because the triplet lifetime in PFO is constant upon blending with PdTPP, the detection is nearly non-perturbing for the continuously generated triplet population. The developed method can be applied to study important processes for lightening and solar cells in organic semiconductors such as triplet–triplet annihilation, fission of singlet excitons, and triplet diffusion.

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